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On the theory of superconductivity in mixed-valence systems

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Abstract : The superconducting properties of some of the mixed-valence compounds have been investigated. A simple two-site model with spin is considered for which the exact solution is possible. Finite temperature specific heat has also been studied. It is shown that the d–d pair density increases with f–f Coulomb repulsion and f-level position. On the other hand, the f–f pair density increases with f–f Coulomb repulsion, but decreases with f-level position. Furthermore, the specific heat appears to be enhanced sharply with the increase of the f–f pair density.

Keywords : Mixed-valence systems, singlet pairing, superconductivity.

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1. Introduction

The mixed-valence (MV) phenomenon in rare-earth systems has been extensively investigated in recent years [1,2]. It is found that the MV compounds $CeRu_2$ [3], $CeCO_2$ [4] and $CeRu_3Si_2$ [5] are superconducting. While $CeRu_2$ and $CeCO_2$ are the strongly mixed-valent materials [6], $CeRu_3Si_2$ is a MV system intermediate between the weakly MV systems like $CeSn_3$ or $CePd_3$ and strongly mixed-valent systems like $CeRu_2$. The spin fluctuation temperature T_{sf} of $CeRu_3Si_2$ is large. In weakly MV systems, T_{sf} is small and none of them was found to be superconducting [7]. The spin fluctuating rate will be large when T_{sf} is high, while the localised f-electron moment will be suppressed and superconductivity favoured. In view of the fact that the MV phenomenon is related to the change of localised f-electron moment and hybridisation between localised f-electron and conduction electrons [7,8], it is reasonable to expect that the hybridisation will play an important role in the superconductivity of the MV system. Besides, it has been shown [9] that both f– and conduction electrons are responsible for superconductivity in MV system. Also, the superconductivity of MV and heavy-fermion (HF) systems are related to each other [9,10].

In this paper, to study the possible superconducting behaviour of MV system, we have considered a two-site model Hamiltonian extended by appropriate attractive interactions. Following experimental results of Rauchschwalbe *et al* [5] and as taken by Feng and Yuan [9], we have assumed singlet pairing terms in our Hamiltonian. As MV and HF superconductors could be described by formally equivalent Hamiltonian, so we have taken the intraband singlet pairing interaction terms according to Zielinski and Matlak [11].

2. Formulation

We consider the Hamiltonian

$$H = H_0 + H_1 \tag{1}$$

where H_0 is the usual MV Hamiltonian and H_1 is the suitable additive pairing interaction term [11] which gives rise to the superconducting behaviour of MV systems,

$$H_0 = \sum_{i,\sigma} \left[E_0 d_{i\sigma}^{+} d_{i\sigma} + E f_{i\sigma}^{+} f_{i\sigma} \right] + U_{ff} \sum_{i} n_{i\uparrow}^{f} n_{i\downarrow}^{f} + \sum_{\substack{i,j,\sigma \\ i \neq j}} V \left(f_{i\sigma}^{+} d_{j\sigma} + d_{j\sigma}^{+} f_{i\sigma} \right) + W \sum_{\substack{i,j,\sigma \\ i \neq j}} d_{i\sigma}^{+} d_{j\sigma} \tag{2}$$

where $i, j = 1, 2$ represents sites, $\sigma = \uparrow, \downarrow$ represents the spin. $d_{i\sigma}^{+}(d_{i\sigma})$ represents a creation (annihilation) operator for a conducting d-electron at the site i with spin σ. $f_{i\sigma}^{+}(f_{i\sigma})$ represents a creation (annihilation) operator for a localised f-electron at the site i with spin σ. $< n_{i\sigma}^{d} >$ represents the occupation number of d-electrons at the site i with spin σ. E_0, E are the d-level energy and f-level energy, respectively, V is the f–d hybridisation interaction parameter, U_{ff} the Coulomb repulsion parameter, and W the hopping interaction parameter between d electrons.

$$H_1 = H_{1f} + H_{1d}, \tag{3}$$

where H_{1f} and H_{1d} are the attractive pairing interaction terms for the f-electrons and the d-electrons respectively.

$$H_{1d} = -G \left[\sum_{i} d_{i\uparrow}^{+} d_{i\downarrow}^{+} d_{i\downarrow} d_{i\uparrow} + \sum_{i,j} \left\{ d_{i\uparrow}^{+} d_{j\downarrow}^{+} d_{i\downarrow} d_{j\uparrow} + d_{i\uparrow}^{+} d_{j\downarrow}^{+} d_{j\downarrow} d_{i\uparrow} + \left(d_{i\uparrow}^{+} d_{i\downarrow}^{+} d_{j\downarrow} d_{i\uparrow} + d_{i\uparrow}^{+} d_{j\downarrow}^{+} d_{i\downarrow} d_{i\uparrow} \right) \right\} \right] \tag{4}$$

and

$$H_{1f} = -G' \sum_{i,j} \left(f_{i\uparrow}^{+} f_{j\downarrow}^{+} f_{i\downarrow} f_{j\uparrow} + f_{i\uparrow}^{+} f_{j\downarrow}^{+} f_{j\downarrow} f_{i\uparrow} \right), \tag{5}$$

where G and G' are the d–d and f–f coupling strengths respectively and $i \neq j$ always in H_1

In eq. (4), term (1) stands for the on-site pairing of d-electrons. Term (2) stands for the pairing of a d-electron if it has hopped from the j-th site to the i-th site with another d-electron hopped from the i-th site to the j-th site. Term (3) stands for the off-site pairing of d-electrons. Term (4) stands for the pairing of a d-electron at the i-th site with another d-electron hopped from the j-th site to the i-th site. Term (5) stands for the pairing of a d-electron at the i-th site with another d-electron hopped from the i-th site to the j-th site.

In eq. (5), term (1) stands for the pairing of an f-electron hopped from the j-th site to the i-th site with another f-electron hopped from the i-th site to the j-th site. Term (2) stands for the off-site pairing of f-electrons.

The attractive interaction part H_1 represents a two-site simplification of the model considered in [11]. Due to strong Coulomb repulsion between f-electrons at the same site, the on-site pairing is excluded for f-electrons, H_1 is written down in the form appropriate for singlet pairing. The representative two-site states with spin are taken in the form [12]

$$\left|n^f_{1\uparrow}\, n^f_{1\downarrow}\, n^d_{1\uparrow}\, n^d_{1\downarrow}\, n^f_{2\uparrow}\, n^f_{2\downarrow}\, n^d_{2\uparrow}\, n^d_{2\downarrow}\right\rangle.$$

There will be 28 basis states and the ground state is taken in the form :

$$|\psi\rangle = \sum_m C_m |\psi_m\rangle. \tag{6}$$

The coefficients C_m are the solutions of the system of equations

$$M \begin{bmatrix} C_1 \\ C_2 \\ \cdot \\ \cdot \\ \cdot \\ C_{28} \end{bmatrix} = 0, \tag{7}$$

where M is a symmetric matrix with the typical element

$$M_{mn} = \left[\langle\psi_m| H |\psi_n\rangle - \lambda\delta_{mn}\right], \tag{8}$$

λ being the lowest solution of the eigenequation

$$\det M = 0 \tag{9}$$

and $|\psi_m\rangle$, $|\psi_n\rangle$ are the basis states.

We have calculated the specific heat

$$C = K\beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2}, \tag{10}$$

where $Z = \sum_\alpha e^{-\beta E_\alpha}$, the sum is taken over all eigenstates, E'_αs are the eigen values, and $\beta = 1/KT$, K being the Boltzmann constant.

3. Result and discussion

Figure 1 shows the variation of $\langle n^{f-f} \rangle$ (f–f pair density) with U_{ff} for different hybridisation strengths. It is seen that with the increase of U_{ff}, the f–f pair density increases. As the value of U_{ff} increases, the probability of finding two f-electrons with opposite spins at the same site decreases. Thus, the possibility of intrasite f–f pair formation decreases with increasing U_{ff}. On the other hand, increase of U_{ff} may increase the probability of finding two f-electrons with opposite spins at neighbouring sites. As only intersite f–f pair formation has been considered here, we get $\langle n^{f-f} \rangle$ increasing with U_{ff}.

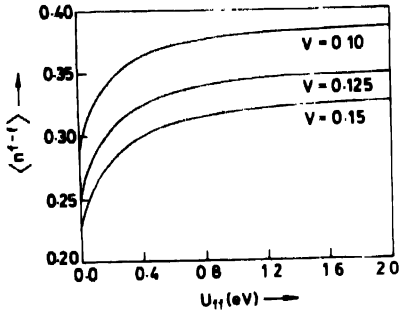

Figure 1. $\langle n^{f-f} \rangle$ as a function of U_{ff} for $T = 0$ K and for various values of V (in eV).
$E_0 = 0$ eV, $E = -0.1$ eV, $W = 0.1$ eV, $G = 0.02$ eV, $G' = 0.04$ eV.

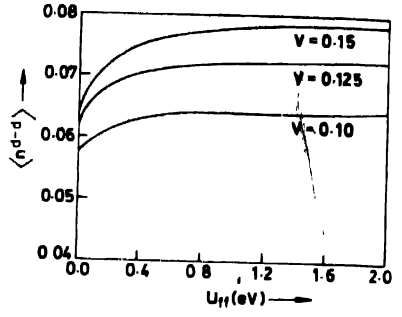

Figure 2. $\langle n^{d-d} \rangle$ as a function of U_{ff} for $T = 0$ K and for various values of V (in eV).
$E_0 = 0$ eV, $E = -0.1$ eV, $W = 0.1$ eV, $G = 0.02$ eV, $G' = 0.04$ eV.

Figure 2 shows the variation of $\langle n^{d-d} \rangle$ (d–d pair density) with U_{ff}. $\langle n^{d-d} \rangle$ is increased with the increase of U_{ff}. Both intra- and inter-site pairing formation have been considered for d-electrons. As U_{ff} increases, decoupling of f-electrons with opposite spins at the same site occurs. This may increase the phase space available for the intrasite pairing formation of d-electrons. It is also apparent from Figures 1 and 2 that the influence of d-electrons becomes more important with increase in hybridisation.

The variation of the f–f pair density with E is presented in Figure 3. $\langle n^{f-f} \rangle$ gradually decreases with the increase of E [13]. This f–f pairing characteristic is possibly due to the fact that with the increase of the f-level position, the f-electron occupation number at every site $\langle n_i^f \rangle$ decreases, thereby further decreasing the tendency to form an f–f pair. Hybridisation has two opposing effects on $\langle n^{f-f} \rangle$. For large negative E (insulating phase), $\langle n^{f-f} \rangle$ decreases with increasing V as explained above. Above –0.07 eV, $\langle n^{f-f} \rangle$ increases with increasing V (metallic phase). In the metallic phase, $\langle n_i^f \rangle$ increases with increasing V, thereby increasing the tendency to form an f–f pair.

Figure 4 shows the variation of the d–d pair density with E. As E increases, d-electron occupation number at each site $\langle n_i^d \rangle$ increases. This makes $\langle n^{d-d} \rangle$ increase with E. Also in the insulating phase, $\langle n^{d-d} \rangle$ increases with V. But, in the metallic phase, $\langle n_i^d \rangle$ decreases with V, thereby decreasing the tendency to form a d–d pair. It is also seen that in the MV region

(the region of f-level energy where the valence transition occurs), substantial amount of both f–f and d–d pairs are present to support superconductivity.

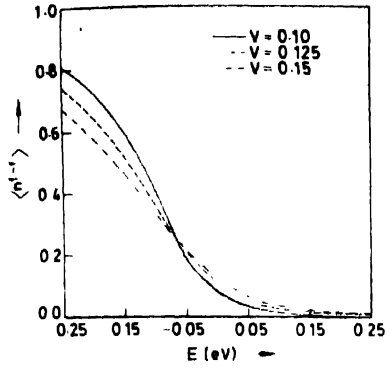

Figure 3. $\langle n^{f-f} \rangle$ as a function of E for $T = 0$ K and for various values of V (in eV).
$E_0 = 0$ eV, $W = 0.1$ eV, $U_{ff} = 2.0$ eV, $G = 0.02$ eV, $G' = 0.04$ eV.

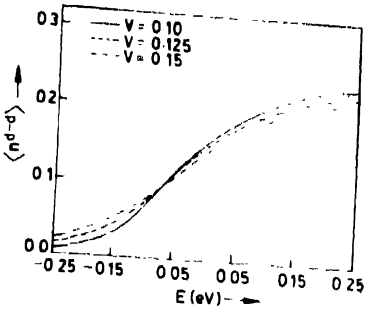

Figure 4. $\langle n^{d-d} \rangle$ as a function of E for $T = 0$ K and for various values of V (in eV)
$E_0 = 0$ eV, $W = 0.1$ eV, $U_{ff} = 2.0$ eV, $G = 0.02$ eV, $G' = 0.04$ eV

Variation of specific heat with temperature is shown in Figure 5. From this figure the specific heat appears to be enhanced sharply with the decrease of f–d hybridisation interaction, which is the main characteristic feature of MV superconductors [5]. This feature also suggests that smaller hybridisation favours superconducting state. However, this result

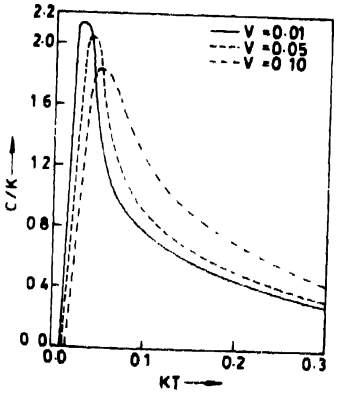

Figure 5. Specific heat per atom vs temperature and for various values of V (in eV).
$E_0 = 0$ eV, $E = -0.1$ eV, $W = 0.2$ eV, $U_{ff} = 2.0$ eV, $G = 0.02$ eV, $G' = 0.04$ eV.

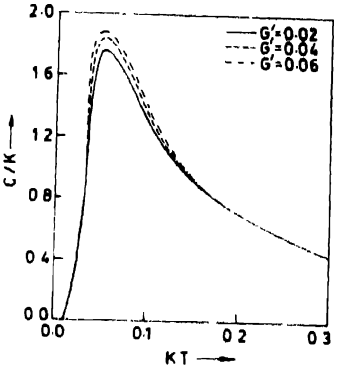

Figure 6. Specific heat per atom vs temperature and for various values of G' (in eV).
$E_0 = 0$ eV, $E = -0.1$ eV, $W = 0.2$ eV, $U_{ff} = 2.0$ eV, $V = 0.1$ eV, $G = 0.02$ eV.

appears to be not fully consistent with the experimental results of Ref. [7]. It is also found that with the increase of hybridisation, the transition temperature of the superconducting state shifts to the higher temperature region.

Curves of specific heat against temperature for different f–f pairing interaction strengths, are presented in Figure 6. It is seen that the specific heat maximum increases with the increase of G' (f–f pairing interaction parameter). It is known that f-electron contribution to specific heat is 10^2–10^3 times more than that of free d-electrons and the high f-electron density of states is responsible for the specific heat maximum [14]. The present observation of specific heat maximum increasing with the increase of the f–f pair density is quite justified. It is also evident from Figure 5 that the f–f pairing appears to have dominant contribution on the superconducting transition compared to that of the d–d pairing.

4. Conclusion

The present investigation on the superconducting properties of MV systems shows that superconductivity is favoured with the increase of f–f Coulomb repulsion interaction. Also, the influence of d-electrons becomes more important with hybridisation. With the increase of E, f–f pair density gradually decreases, but d–d pair density increases. In the mixed-valent region, substantial amount of both f–f and d–d pairs are present to support superconductivity. Results of specific heat show that with hybridisation the transition temperature of the superconducting state shifts to the higher temperature region. Also, the f–f pairing appears to have dominant contribution on the superconducting transition. But, the present observation that smaller hybridisation favours superconducting state, appears to contradict available experimental results. Further study in this regard is going on.

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